

F3



(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention
of the grant of the patent:
17.04.2002 Bulletin 2002/16

(51) Int Cl.7: **A62C 35/02, C06B 45/10,
A62C 39/00, C06D 5/06**

(21) Application number: **94920166.9**

(86) International application number:
PCT/US94/06622

(22) Date of filing: **13.06.1994**

(87) International publication number:
WO 95/00205 (05.01.1995 Gazette 1995/02)

(54) **APPARATUS AND METHOD FOR SUPPRESSING A FIRE**
VORRICHTUNG UND VERFAHREN ZUR FEUERBEKÄMPFUNG
APPAREIL ET PROCEDE POUR COMBATTRE LE FEU

(84) Designated Contracting States:
DE FR GB IT

(30) Priority: **24.06.1993 US 82137**
25.05.1994 US 248932

(43) Date of publication of application:
10.04.1996 Bulletin 1996/15

(73) Proprietor: **OLIN CORPORATION**
New Haven, CT 06511-1837 (US)

(72) Inventors:
• **GALBRAITH, Lyle, D.**
Redmund, WA 98052 (US)
• **HOLLAND, Gary, F.**
Snohomish, WA 98290 (US)

• **POOLE, Donald, R.**
Woodinville, WA 98072 (US)
• **MITCHELL, Robert, M.**
Issaquah, WA 98027 (US)

(74) Representative: **Klunker . Schmitt-Nilson . Hirsch**
Winzererstrasse 106
80797 München (DE)

(56) References cited:

US-A- 798 142	US-A- 1 119 799
US-A- 1 648 397	US-A- 2 530 633
US-A- 2 838 122	US-A- 3 785 674
US-A- 3 901 747	US-A- 4 194 571
US-A- 4 276 938	US-A- 4 319 640
US-A- 4 601 344	US-A- 4 637 472
US-A- 5 035 757	

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 0 705 120 B1

Description

[0001] This invention relates to an apparatus and a method for suppressing a fire as well as to a gas generating composition. More particularly, a gas generator produces an elevated temperature first gas which interacts with a vaporizable liquid to generate a second gas having flame suppressing capabilities.

[0002] Fire involves a chemical reaction between oxygen and a fuel which is raised to its ignition temperature by heat. Fire suppression systems operate by any one or a combination of the following: (i) removing oxygen, (ii) reducing the system temperature, (iii) separating the fuel from oxygen, and (iv) interrupting the chemical reactions of combustion. Typical fire suppression agents include water, carbon dioxide, dry chemicals and the group of halocarbons collectively known as Halons.

[0003] The vaporization of water to steam removes heat from the fire. Water is an electrical conductor and its use around electrical devices is hazardous. However, in non-electrical situations, when provided as a fine mist over a large area, water is an effective, environmentally friendly, fire suppression agent.

[0004] Carbon dioxide (CO₂) gas suppresses a fire by a combination of the displacement of oxygen and absorption of heat. Carbon dioxide gas does not conduct electricity and may safely be used around electrical devices. The carbon dioxide can be stored as compressed gas, but requires high pressure cylinders for room temperature storage. The cylinders are heavy and the volume of compressed gas limited. Larger quantities of carbon dioxide are stored more economically as a liquid which vaporizes when exposed to room temperature and atmospheric pressure.

[0005] When exposed to room temperature and atmospheric pressure, the expansion characteristics of liquid CO₂ are such that approximately one third of the vessel charge freezes during the blow down process. Only about two thirds of the CO₂ is exhausted in a reasonable time. The remainder forms a dry ice mass which remains in the storage vessel. While the dry ice eventually sublimates and exits the vessel, the sublimation period is measured in hours and is of little use in fire suppression.

[0006] The problem with liquid carbon dioxide based fire suppression systems is worse when low temperature operation is required. At -55°C, the vapor pressure of carbon dioxide is about 0.48 MPa (70 psig) (compared to 4.8 MPa (700 psig) at 20°C) which is totally inadequate for rapid expulsion.

The vessel freeze-up problem is worse. About 50% of the liquid carbon dioxide solidifies when exposed to -55°C and atmospheric pressure.

[0007] Improved carbon dioxide suppression systems add pressurized nitrogen to facilitate the rapid expulsion of carbon dioxide gas at room temperature. The pressurized nitrogen does not resolve the freezing problem at low temperatures and at upper service extremes, about 70°C, the storage pressure is extremely high, dictating the use of thick, heavy, walled storage vessels.

[0008] Chemical systems extinguish a fire by separating the fuel from oxygen. Typical dry chemical systems include sodium bicarbonate, potassium bicarbonate, ammonium phosphate and potassium chloride. Granular graphite with organic phosphate added to improve effectiveness, known as G-1 powder, is widely used on metal fires. Other suitable dry compounds include sodium chloride with tri-calcium phosphate added to improve flow and metal stearates for water repellency, dry sand, talc, asbestos powder, powdered limestone, graphite powder and sodium carbonate. Dry chemical systems are delivered to a fire combined with a pressurized inert gas or manually such as with a shovel. The distribution system is inefficient for large fires and a significant amount of time is required to deliver an effective quantity of the dry powder to suppress a large fire.

[0009] US-A-1,468,397 discloses a fire extinguisher comprising a container charged with liquid carbon dioxide, a cell filled with a combustible mixture, and a tank filled with a solution of ammonium carbonate in water. The fire extinguisher may be operated manually or automatically. When operated manually, the carbon dioxide container is opened and carbon dioxide enters into the tank, forcing out the ammonium carbonate solution. When operated automatically, the combustible mixture is burned, and hot gases are released into the environment while heating the ammonium carbonate solution in the tank. When the solution is heated, ammonia, carbon dioxide and steam are released. The fire extinguisher does not generate a high temperature gas selected from the group consisting of nitrogen, carbon dioxide, water vapour and mixtures thereof.

[0010] US-A-4,601,344 discloses a method of extinguishing a fire wherein a gas generating composition comprising glycidyl azide polymer and a high nitrogen content additive is ignited in order to generate nitrogen gas. The gas generating compositions, however, do not only produce nitrogen, but also hydrogen, carbon monoxide and methane, which gases are flammable on mixing with air.

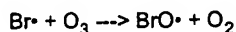
[0011] US-A-3,901,747 discloses a pyrotechnic composition for generating a low-flame temperature, non-toxic gas, the composition comprising a carbonaceous material, aluminium or magnesium as a fuel, an inorganic oxidizer and a binder-coolant, e.g. a mixture of magnesium carbonate and magnesium hydroxide. A nitrogen rich powder fuel is not disclosed.

[0012] The most efficient fire suppression agents are Halons. Halons are a class of brominated fluorocarbons and are derived from saturated hydrocarbons, such as methane or ethane, with their hydrogen atoms replaced with atoms

of the halogen elements bromine, chlorine and/or fluorine. This substitution changes the molecule from a flammable substance to a fire extinguishing agent. Fluorine increases inertness and stability, while bromine increases fire extinguishing effectiveness. The most widely used Halon is Halon 1301, CF_3Br , trifluorobromomethane. Halon 1301 extinguishes a fire in concentrations far below the concentrations required for carbon dioxide or nitrogen gas. Typically, a Halon 1301 concentration above about 3.3% by volume will extinguish a fire.

[0013] Halon fire suppression occurs through a combination of effects, including decreasing the available oxygen, isolation of fuel from atmospheric oxygen, cooling and chemical interruption of the combustion reactions. The superior fire suppression efficiency of Halon 1301 is due to its ability to terminate the runaway reaction associated with combustion. The termination step is catalytic for Halon 1301 due to the stability of bromine radicals ($\text{Br}\cdot$) formed when Halon 1301 is disposed on a combustion source.

[0014] When unreacted Halon 1301 migrates into the stratosphere, sunlight breaks down the Halon 1301 forming bromine radicals. $\text{Br}\cdot$ then reacts to consume ozone in an irreversible manner.



[0015] In view of the current recognition that ozone depletion is a serious environmental problem, a move is on to identify: (i) fire suppression agents having a less severe environmental impact than Halon and (ii) devices to deliver these more environmentally friendly agents.

[0016] Accordingly, it is an object of the invention to provide a fire suppression apparatus for effectively delivering a fire suppressant which is less environmentally hazardous than Halon. It is a feature of the invention that the apparatus effectively delivers both liquid and solid fire suppressants. It is an advantage of the invention that the apparatus does not require significantly more space than Halon fire suppression apparatus. A further advantage of the invention is that both high and low vapor pressure liquids are effectively stored, vaporized and delivered in gaseous form.

[0017] Furthermore, it is an object of the invention to provide a gas generating composition suitable for use in the fire suppression apparatus.

[0018] In accordance with the invention, there is provided an apparatus for suppressing a fire comprising a gas generator containing a propellant; (b) a chamber containing a vaporizable liquid or particles of a flame suppressing material or a mixture of water and ice; (c) a passageway between said chamber and said fire. An apparatus having these features is known from US-A-1,648,397. The apparatus of the present invention is characterized by (d) a passageway between said gas generator and said chamber; (e) the gas generator generating a high temperature gas selected from the group consisting of nitrogen, carbon dioxide, water vapor and mixtures thereof.

[0019] When activated, the apparatus suppresses a fire by generating, by means of the gas generator, an elevated temperature first gas. A first liquid is substantially vaporized by interaction with the first gas generating a second gas having flame suppressing capabilities, the second gas is then directed at the fire. Alternatively, a solid flame suppressant may be utilized instead of the first liquid.

[0020] In another embodiment of the invention, the first gas is an effective flame suppressant such as CO_2 , N_2 or water vapor. The first gas may be used directly as a flame suppressant or combined with the second gas for flame suppression.

[0021] Accordingly, there is provided in accordance with the invention an apparatus for suppressing a fire, having a gas generator which generates a high temperature gas and having a passageway between said gas generator and said fire. An apparatus having these features is known from US-A-1,648,397. The apparatus of the present invention is characterized in that said gas generator contains a compacted mixture of a nitrogen rich powder fuel; a powder oxidizer; and a powder coolant, and said high temperature gas being selected from the group consisting of nitrogen, carbon dioxide, water vapor and mixtures thereof.

[0022] Furthermore, there is provided a gas generating composition comprising a nitrogen rich powder fuel; a powder oxidizer; and magnesium carbonate powder, wherein combustion of said nitrogen rich powder fuel, powder oxidizer and magnesium carbonate powder generates particulate and gas selected from the group consisting of nitrogen, carbon dioxide, water vapor, and mixtures thereof.

[0023] In particular, there is provided such gas generating composition comprising 5-aminotetrazole, strontium nitrate and from 20% to 95% by weight magnesium carbonate.

[0024] The above stated objects, features and advantages will become more apparent from the specification and drawings which follow.

[0025] Figure 1 illustrates in cross-sectional representation an apparatus for vaporizing a liquid to a flame suppressing gas in accordance with a first embodiment of the invention.

[0026] Figure 2 illustrates in cross-sectional representation an apparatus for vaporizing a liquid to a flame suppressing gas in accordance with a second embodiment of the invention.

[0027] Figure 3 illustrates in cross-sectional representation an apparatus for delivering a dry chemical flame sup-

pressant to a fire.

[0028] Figure 4 illustrates in cross-sectional representation a carbon dioxide producing gas generator.

[0029] Figure 5 graphically illustrates increasing the magnesium carbonate content in the gas generator reduces the formation of corrosive effluent.

[0030] Figure 6 graphically illustrates the relationship between pressure and density for ice and water.

[0031] Figure 7 illustrates in cross sectional representation a water based fire suppression system in accordance with the invention.

[0032] Figure 1 shows in cross-sectional representation a fire suppression apparatus 10 in accordance with a first embodiment of the invention. A gas generator 12 containing a suitable solid propellant 14 delivers an elevated temperature first gas 16 to a vaporizable liquid 18 contained in a chamber 20. A first conduit 22 provides a passageway between the gas generator 12 and the chamber 20. The first gas 16 interacts with the vaporizable liquid 18 converting the liquid to a second gas 24. By proper selection of the vaporizable liquid 18, the second gas has flame suppressing capabilities. A second conduit 26 directs the second gas 24 to a fire. An optional aspirator 28 uniformly distributes the second gas 24 over a wide area.

[0033] The fire suppression apparatus 10 is permanently mounted in a ceiling or wall of a building, aircraft or other suitable structure or vehicle. A sensor 30 detects the presence of a fire. Typically, the sensor 30 detects a rise in temperature or a change in the ionization potential of air due to the presence of smoke. On detecting a fire, the sensor 30 transmits an activating signal to a triggering mechanism 32. The activating signal may be a radio pulse, electric pulse transmitted by wires 34 or other suitable means.

[0034] The triggering mechanism 32 is any device capable of igniting the solid propellant 14. One triggering mechanism is an electric squib. The electric squib has two leads interconnected by a bridge wire, typically 0.076mm-0.10mm (3-4 mil) diameter nichrome. When a current passes through the leads, the bridge wire becomes red hot, igniting an adjacent squib mixture, typically, zirconium and potassium perchlorate. The ignited squib mixture then ignites an adjacent black powder charge, creating a fire ball and pressure shock wave which ignites the solid propellant 14 housed within the gas generator 12.

[0035] The gas generator 12 contains a solid propellant 14 which on ignition generates a large volume of a high temperature gas containing fire suppressing fluids such as carbon dioxide, nitrogen and water vapor. Depending on the selection of the vaporizable liquid and the type of fire anticipated as requiring suppression, the gas is generated for a period of time ranging from a few milliseconds to several seconds. One particularly suitable gas generator is the type used in automotive air bags as described in U.S. Patent No. 3,904,221 to Shiki et al. A housing 36 supports the solid propellant 14 and directs an explosive shock wave in the direction of the vaporizable liquid 18. Typical materials for the housing 36 include aluminum alloys and stainless steel.

[0036] The preferred solid propellant 14 is a combustible mixture which generates a copious amount of high temperature gas. The chemical reactions converting the propellant to the first gas generally do not occur efficiently at temperatures below about 1093°C (2000°F). The gas yield in moles per 100 grams of propellant should be in excess of about 1.5 moles and preferably in excess of about 2.0 moles. The propellants are generally a mixture of a nitrogen rich fuel and an oxidizing agent in the proper stoichiometric ratio to minimize the formation of hydrogen and oxygen. The preferred fuels are guanidine compounds, azide compounds and azole compounds.

[0037] Two preferred solid propellants are "RRC-3110" and "FS-01" (both available from Olin Aerospace Company of Redmond, Washington, United States of America). The compositions (in weight percent) of these propellants are:

RRC-3110	
5-Aminotetrazole	28.62%
Strontium nitrate	57.38%
Clay	8.00%
Potassium 5-Aminotetrazole	6.00%

[0038] When ignited, RRC-3110 generates H_2O , N_2 and CO_2 as well as SrO , $SrCO_3$ and K_2CO_3 particulate.

FS-01	
5-Aminotetrazole	29.20%
Strontium nitrate	50.80%
Magnesium carbonate	20.00%

[0039] When ignited, FS-01 generates H_2O , N_2 and CO_2 as well as SrO , $SrCO_3$ and MgO particulate.

[0040] Another useful propellant composition is:

Guanidine nitrate	49.50%
Strontium nitrate	48.50%
Carbon	2.00%

[0041] When ignited, this composition releases a mixture of H_2O , N_2 and CO_2 gases along with SrO and $SrCO_3$ particulate solids.

[0042] Propellants which generate KCl salt are also suitable. KCl is effective in suppressing fires, but the corrosive nature of the salt limits the application of these propellants. Two such propellants are:

5-Aminotetrazole	30.90%
Potassium perchlorate	44.10%
Magnesium carbonate	25.00%

[0043] When ignited, this propellant generates H_2O , N_2 and CO_2 gas as well as KCl and MgO particulate.

Potassium chlorate	61.0%
Carbon	9.0%
Magnesium carbonate	30.0%

[0044] When ignited, this propellant generates CO_2 as the only gas and KCl and MgO particulate.

[0045] Another suitable propellant generates nitrogen gas and solid slag which remains in the housing 36, only the gas is delivered to the vaporizable liquid eliminating contamination of the area by the solid particulate.

Sodium azide	59.1%
Iron oxide	39.4%
Potassium nitrate	1.0%
Carbon	0.5%

[0046] When ignited, this propellant generates N_2 gas and slag which is not discharged from the housing.

[0047] The propellants useful in the apparatus of the invention are not limited to the five specified above. Any solid propellant capable of generating similar gaseous products at high velocity and high temperature is suitable.

[0048] The most preferred propellants contain magnesium carbonate as a suppressing agent. The magnesium carbonate may be combined with a fuel, as in the FS-01 propellant, combined with other suppressing agents or utilized as a single component fire suppressing propellant. The magnesium carbonate endothermically decomposes to carbon dioxide (a good oxygen displacer) and magnesium oxide (a good heat sink and coolant).

[0049] Suitable propellants contain from that amount effective to extinguish a fire up to about 95% by weight magnesium carbonate and the balance being the mixture of a fuel and an oxidizer. Preferably, the propellant contains from about 20% to about 70% by weight magnesium carbonate and most preferably, from about 30% to about 60% by weight magnesium carbonate.

[0050] When the magnesium carbonate content is low, propellants containing strontium nitrate yield effluent rich in strontium oxide. On exposure to atmospheric moisture, this yields extremely basic solutions that are corrosive to aluminum and other materials utilized in aircraft manufacture. With reference to Figure 5, applicant has determined a minimum magnesium carbonate content of about 35% is desired to minimize the corrosion potential.

[0051] Propellant additives such as magnesium carbonate act as endothermic heat sinks and carbon dioxide generators. These effects decrease the corrosivity of propellant effluent by minimizing the amount of strontium oxide generated. Figure 5 graphically illustrates the composition of the gaseous effluent generated by igniting the FS-01 fuel with varying amounts of magnesium carbonate present. The strontium oxide content is identified by reference line 80. Approximately 35 weight percent magnesium carbonate is required to achieve an essentially strontium oxide free effluent.

[0052] Strontium carbonate (reference line 82) and magnesium oxide (reference line 84) form compounds with a pH near 7 when exposed to atmospheric moisture and generally do not cause significant corrosion.

[0053] A preferred propellant contains a nitrogen rich fuel, an oxidizer and magnesium carbonate. Suitable propellants include modifications of FS-01 containing 5-aminotetrazole and an oxidizer, such as strontium nitrate, potassium perchlorate or mixtures thereof. The fuel to oxidizer ratio, by weight, is from about 1:1 to about 1:2. Combined with the

fuel and oxidizer is from about 20% to about 70% by weight magnesium carbonate (measured as a percentage of the propellant/magnesium carbonate/additives compacted mixture). The propellant may also contain additives such as clay (to improve molding characteristics) or graphite (to improve flow characteristics).

[0054] The propellant is a mixture of compacted powders. If all powder components are approximately the same size, the burn rate is unacceptably low. Preferably, the propellant is a mixture of relatively large magnesium carbonate particles having an average particle diameter of from about 150 μm (microns) to about 200 μm (microns) and relatively small fuel and oxidizer particles having an average particle diameter of from about 50 μm (microns) to about 75 μm (microns). The larger magnesium carbonate particles form discrete coolant sites and do not reduce the propellant burn rate as drastically as when all components are approximately the same size.

[0055] The solid propellant may be required to generate the gas over a time ranging from about 30 milliseconds to several seconds. Typically, a short "burn time" is required in an explosive environment while a longer burn time is required in a burning environment. If a short burn time is desired, the propellant is in the form of tablets, typically on the order of 1 centimeter in diameter by about one half centimeter thick. Increasing the pellet size increases the burn time. For a burn time of several seconds, the gas generator contains a single propellant slug compression molded into the housing.

[0056] Referring back to Figure 1, to prevent the housing 36 from melting during ignition of the solid propellant 14, a cooling material 38 may be disposed between the housing 36 and solid propellant 14. One cooling material is granular magnesium carbonate which generates carbon dioxide when heated above 150°C (300°F). One mole of MgCO_3 will produce one mole of CO_2 plus one mole of MgO , which remains in the housing 36 in the form of a slag. Small amounts of MgO dust may be exhausted during ignition of the solid propellant.

[0057] To prevent contamination of the chamber 20 by the solid propellant 14 prior to ignition, a first rupture diaphragm 40 isolates the vaporizable liquid 18. The isolation diaphragm 40 is ruptured by the pressure of the shock wave. No active device such as a disk rupturing detonator is required. To prevent the generation of mechanical debris, the isolation diaphragm 40 may have score lines and hinge areas to open in a petal like fashion.

[0058] The first conduit 22 forms a passageway to communicate the first gas 16 to the vaporizable liquid 18. The first gas 16 is superheated and traveling at high velocity. Interaction of the first gas and the vaporizable liquid 18 vaporizes the liquid, generating a second gas 24. The second gas 24 ruptures the second isolation diaphragm 42 and is expelled as a fire suppressing gas, preferably through aspirator 28.

[0059] The selection of the vaporizable liquid 18 is based on a desire that the second gas 24 be less reactive with atmospheric ozone than Halon. The vaporizable liquid 18 contains no bromine, and preferably also no chlorine. Preferred groups of vaporizable liquids 18 include fluorocarbons, molecules containing only a carbon-fluorine bond and hydrogenated fluorocarbons, molecules containing both carbon-hydrogen and carbon-fluorine bonds. Table 1 identifies preferred fluorocarbons and hydrogenated fluorocarbons and their vaporization temperatures. For comparison, the data for Halon 1301 is also provided.

TABLE 1

System	Formula	Vaporization Temperature (°C)	Vaporization Pressure Room Temperature	
			(MPa)	(psi)
HFC-32	CH_2F_2	-52	0.83	120
HFC-227	$\text{CF}_3\text{CHFCH}_3$	-15	0.41	59
HCFC-22	CHClF_2	-41	0.96	139
HCFC-134A	$\text{CF}_3\text{CH}_2\text{F}$	-27	0.57	83
FC-116	CF_3CF_3	-78	3.2	465
HCFC-124	CHClFCF_3	-12	0.42	61
HFC-125	$\text{CF}_3\text{CF}_2\text{H}$	-48	1.3	195
FC31-10	C_4F_{10}	-2	—	—
FC-C318	$(\text{CF}_2)_4$	-4	—	—
HF-23	CF_3H	-82	4.8	700
HCFC-123	$\text{CF}_3\text{CCl}_2\text{H}$	-28	0.09	13
FC-218	$\text{CF}_3\text{CF}_2\text{CF}_3$	-36	0.83	120
FC-614	C_6F_{14}	+56	—	—
HALON 1301	CF_3Br	-58	1.5	220

[0060] The most preferred fluorocarbons and hydrogenated fluorocarbons are those with the higher boiling points

and lower vapor pressures. The higher boiling point reduces the pressure required to store the vaporizable liquid 18 as a liquid. The lower vapor pressures increase the rate of conversion of the vaporizable liquid to fire suppressing gas on ignition. Particularly suitable are HFC-227, FC-31-10, FC-318 and FC-218.

[0061] Unsaturated or alkene halocarbons have a low vapor pressure and a relatively high boiling point. These unsaturated molecules contain a carbon-carbon double bond, together with a carbon-fluorine bond, and in some cases, a carbon-hydrogen bond. The unsaturation causes these compounds to be considerably more photosensitive than a saturated species, leading to significant photochemical degradation in the lower atmosphere. The low altitude photo-degradation may lessen the contribution of these compounds to stratospheric ozone depletion. Through the use of an unsaturated halocarbon in the fire suppression apparatus of the invention, it is possible that bromine containing compounds may be tolerated.

[0062] Representative haloalkenes have a boiling point of from about 35°C to about 100°C and include 3-bromo-3,3-difluoro-propene, 3-bromo-1,1,3,3-tetrafluoropropene, 1-bromo-3,3,3-trifluoro-1-propene, 4-bromo-3,3,4,4-tetrafluoro-1-butene and 4-bromo-3,4,4-trifluoro-3-(trifluoromethyl)-1-butene, as well as homologues, analogs and related compounds.

[0063] One disadvantage with the fluorocarbons and hydrogenated fluorocarbons, whether saturated or unsaturated, is the generation of small amounts of hydrogen fluoride when the vapor contacts a fire. Hydrogen fluoride is corrosive to equipment and hazardous to personnel.

[0064] The significant heat and pressure conducted by the first gas 16 permits the use of liquid carbon dioxide or water as the vaporizable liquid 18. The expansion problem identified above for nonenergetically discharged liquid carbon dioxide is eliminated by the superheating effect of the first gas 16. Water is converted to a fine mist of steam on interaction with the first gas and is highly effective for flame suppression.

[0065] As water is such an effective fire suppression media when delivered in the form of fine droplets, a mist or as a superheated steam to a fire, it is one of the most favored fluids for use in this gas generation concept. However, because water freezes at a temperature of 0°C (32°F), a means must be incorporated to either suppress the freezing point or the design of the gas generator must be such that it can operate effectively with the water frozen solid.

[0066] Most military and commercial applications require that fire suppression equipment operate effectively over a temperature range of -54°C to +71°C (-65°F to +160°F). Many additives such as ammonia, alcohol, glycols, and salts are capable of suppressing the water freezing point to below -54°C (-65°F), but a considerable portion of the mixture becomes the additive. Most additives are flammable or corrosive, degrading the effectiveness and desirable features of a water system when freezing point depressants are present in the water.

[0067] To maintain the desirable features of water as the agent for the gas generator driven system, the system can be designed to operate effectively over the desired -54°C to +71°C (-65°F to +160°F) temperature range even if the water has frozen solid.

[0068] Figure 6 graphically illustrates the relationship between density and temperature for water and ice at atmospheric pressure, moderate increased pressure and moderate vacuums. At slightly over 0°C (+32°F), the density of liquid water is 1.0 g/cm³ (62.40 lbm/ft³). If the temperature of the water is reduced just below 0°C (32°F), the water will freeze to ice and expand considerably in volume. The density of ice at 0°C (+32°F) is 0.92 g/cm³ (357.50 lbm/ft³).

[0069] Below 0°C, the density of ice increases as the temperature is decreased as illustrated by reference line 86. Above 0°C, the density of water decreases as the temperature is increased as illustrated by reference line 88.

[0070] Figure 7 shows in cross sectional representation a water based fire suppression system 90 that accommodates the expansion of ice due to freezing the water. The fire suppression system 90 includes a solid propellant gas generator 12 described above and previously illustrated in Figure 1. The gas generator 12 communicates with a tank 92 by a passageway formed by a first conduit 93. The tank 92 contains a mixture of water 94 and ice 96. The tank 92 has a volume larger than the volume of ice that would be contained if all the water 94 was frozen.

[0071] The gas generator 12 provides sufficient thermal energy to heat the ice 96 to the freezing point and melt the ice by directing a hot gas 98 produced by the gas generator 12 in the direction of the ice 96. Nozzle 100 may be provided to direct the flow of the hot gas 98 to impinge the mixture of ice and water inducing turbulence to assure good mixing and vaporization of the water.

[0072] Heating of the ice 96 and water 94 is further enhanced by the use of a propellant which exhausts a significant percent of solids into the tank 92 along with the hot gases 98. Preferably, at least about 20% by weight, and most preferably, at least about 40% by weight of the effluent is solid particles.

[0073] The tank 92 is designed to facilitate unrestricted expansion of ice 96. There are no pockets or cavities to interfere with the ice growth. Mechanical parts of the gas generator are not in the path of ice growth to minimize breaking of the mechanical parts.

[0074] The temperature of the generated gases is preferably in excess of about 925°C (1700°F) and typically exceeds 1093°C (2000°F). The gas generator is preferably selected so that the exhaust contains at least 20% and preferably in excess of about 40% by weight hot solid particulate (i.e. MgO, etc.). This exhaust stream provides a very effective means for rapidly melting the ice.

[0075] Another feature of the water based fire suppression system 90 is that the ullage space 102 above the water 94 and ice 96 is sufficiently large to assure that the resulting pressure of the hot gases 98 exhausting into the tank 92 do not produce a pressure sufficient to rupture the outlet burst disc 104, typically about 13.8 MPa (2000 psig). The system is designed to require additional hot gases 98 from the gas generator 92 to be added to superheat the vaporized water before the outlet disc 104 is ruptured and flow commences.

[0076] Once the outlet disc 104 has been ruptured, the continuing flow of gases 98 from the gas generator 12 creates significant turbulence and mixing of the water 94 within the tank 92 vaporizing the water to produce steam 106. Depending upon the particular fire suppressing application, it may be desirable to design the unit to produce low quality steam at low temperatures or superheated steam at higher temperatures. Any temperature and steam quality can be produced by the proper proportioning of the water and solid propellant used in the system. The steam 106 is directed at the fire through a second passageway formed by a second conduit 107.

[0077] It may sometimes be desirable to incorporate an additive 108 to the water 94 to reduce the heat of fusion of the ice 96. Effective chemical additives include polyvinyl alcohol and water soluble polymers such as methyl cellulose, added to the water in concentrations of less than about 15% by volume. The additives 108 also tend to form a viscous gel when properly added to the water. This higher viscosity working fluid is much less prone to leaking from the tank 92 than water.

[0078] In a second embodiment of the invention, the fire suppression apparatus 50 is as illustrated in cross-sectional representation in Figure 2. The elements of the second fire suppression apparatus 50 are substantially the same as those illustrated in Figure 1 and like elements are identified by like Figure numerals. Typically the solid propellant 14 generates solid particulate along with the first gas. Particulate may also be generated by other components of the fire suppression apparatus such as the magnesium carbonate cooling layer 38. If the environment in which the flame suppression apparatus 50 is located would be detrimentally affected by the presence of solid particulate, a bladder 52 may be disposed between the gas generator 12 and the chamber 20. The energetic first gas 16 forcedly deforms the flexible bladder 52, generating a shock wave vaporizing the vaporizable liquid 18 and generating the second gas 24. The bladder 52 may be any suitable material such as a high temperature elastomer.

[0079] This second embodiment does not superheat the vaporizable liquid 18 as effectively as the first embodiment. The transfer of heat through the elastomeric material 52 is limited. Accordingly, lower boiling point vaporizable liquids such as HFC-32, FC-116 and HF-23 are preferred.

[0080] In a third embodiment of the invention, a solid flame suppressant may be utilized as illustrated by the flame suppression apparatus 60 of Figure 3. The flame suppression apparatus 60 illustrated in cross-sectional representation is similar to the earlier embodiments and like elements are identified by like reference numerals, while elements performing a similar function are identified by primed reference numerals. The chamber 20' is packed with small diameter, on the order of from about 5 to about 100 μm (micron), and preferably from about 10 to about 50 μm (micron), particles 62 of any effective flame suppressing material. Suitable materials include potassium bicarbonate, sodium bicarbonate, ammonium phosphate, potassium chloride, granular graphite, sodium chloride, magnesium hydroxide, calcium hydroxide, strontium hydroxide, barium hydroxide, aluminum hydroxide, magnesium carbonate, potassium sulfate, sand, talc, powdered limestone, graphite powder, sodium carbonate, strontium carbonate, calcium carbonate and magnesium carbonate. These and other suitable materials may be mixed with boron oxide as disclosed in U.S. Patent No. 4,915,853 to Yamaguchi.

[0081] In the preceding embodiments of the invention, the flame suppression apparatus has been described in terms of a superheated gas interacting with a vaporizable liquid. The superheated gas is predominantly nitrogen, carbon dioxide and water vapor, all effective fire suppressants. In certain applications, it is preferred to omit the vaporizable liquid and discharge the flame suppressing gases generated by the solid propellant directly onto the fire. A carbon dioxide producing gas generator 70 is illustrated in cross-sectional representation in Figure 4.

[0082] The carbon dioxide producing gas generator 70 is similar to the gas generators described above. An electric squib 32 activates an energetic mixture of a solid propellant 14. On ignition, the solid propellant 14 ignites a magnesium carbonate containing propellant 72 generating MgO , CO_2 , N_2 , and water vapor. A perforated screen 74 separates the propellants from the housing of the generator 12. A magnesium carbonate cooling bed 76 is disposed between the housing and propellants and on heating generates additional CO_2 . The propellant 72 may contain other fire suppressing agents, in addition to magnesium carbonate, either alone or in combination. Suitable fire suppressing agents include magnesium hydroxide, calcium hydroxide, strontium hydroxide, barium hydroxide and aluminum hydroxide.

[0083] The following examples illustrate the effectiveness of the flame suppressing apparatus of the invention.

EXAMPLES

Example 1

[0084] The gas generator 70 is an efficient apparatus for delivering a low molecular weight inerting agent, such as

CO₂, N₂, or water vapor, to a fire. The weight of the apparatus and propellant compares favorably to the weight of a halon based fire suppression system.

Gas Generator Characteristics

[0085]

Length - 42.24 centimeters (16.63 inches)
 Diameter - 13.97 centimeters (5.50 inches)
 Displaced external volume - 0.0065 meter³ (395 inch³)
 FS-O1 propellant load - 2.01 kilograms (4.437 pounds), generates 1.41 kilograms (3.10 pounds) of CO₂, N₂, and water vapor
 MgCO₃ coolant load - 6.00 kilograms (13.21 pounds), generates 3.13 kilograms (6.894 pounds) of CO₂
 Total inerting gas produced- 4.54 kilograms (10.00 pounds)
 Estimated weight of total system - 11.8 kilograms (26.10 pounds)

Gas Generator Materials

[0086]

Housing 12 - Aluminum alloy 6061-T6
 Solid propellant 14 - BKNO₃
 FS-O1 propellant 72 - in pellet form, size of pellets based on desired burn time, about 1 centimeter diameter by 0.5 centimeter thick tablets provide a 30 millisecond burn.
 MgCO₃ coolant bed 76 - granular
 Perforated retaining screen 74 has 1.27 millimeter (0.050 inch) perforations.

[0087] This system will produce about 4.54 kilograms (10 pounds) of CO₂, N₂, and water vapor, weigh about 11.8 kilograms (26.10 pounds) and occupy 0.0065 meter³ (395 inch³) of space. By comparison, a Halon 1301 system containing 4.54 kilograms (10 pounds) of fire suppressant weighs about 8.6 kilograms (19 pounds) and occupies 0.0065 meter³ (365 inch³) of space. While the system of the invention is only slightly larger and heavier than the Halon system, other Halon replacement systems are predicted to increase the weight by a factor of 2 or 3.

Example 2

[0088] The corrosive action of saturated solutions of the effluent components on materials commonly utilized in aircraft was evaluated. An aqueous solution saturated with the effluent was prepared and the pH measured. Various materials were then exposed to a 50% relative humidity atmosphere of each saturated solution. After a 30 day exposure, the coupons were analyzed for corrosion pits. Table 2 illustrates the benefit of removing strontium oxide from the effluent.

[0089] It is apparent that there has been provided in accordance with this invention an apparatus and method for suppressing a fire which fully satisfies the objects, means and advantages set forth hereinbefore. While the invention has been described in combination with specific embodiments thereof, it is evident that many alternatives, modifications and variations will be apparent to those skilled in the art in light of the foregoing description. Accordingly, it is intended to embrace all such alternatives, modifications and variations as fall within the spirit and broad scope of the claims.

TABLE 2

	Composition	MgO	SrCO ₃	FS-01 40% MgCO ₃	FS-01 20% MgCO ₃	3110	SrO	KOH
pH (measured) Sat. Aq. Soln.		8.5	9.0	9.0	11.0	11.5	13.5	13.5
A06061 chromated surface	Mg 0.8-1.2 Si 0.4-0.8 Cu 0.15-0.40 Cr 0.04-0.34 Al Balance	not analyzed	not analy- zed	0	uniform pitting	uniform pitting	uni- form pit- ting	uni- form pit- ting
A07075 anodized surface	Zn 5.1-6.1 Mg 2.1-2.9 Cu 1.2-2.0 Cr 0.18-0.35 Al Balance	0	0	0	0	0	3	3
A07030 anodized surface	Zn 2.7-3.3 Mg 1.4-1.8 Mn 0.4-0.6 Cr 0.2-0.4 Al Balance	0	0	0	2	5	uni- form pit- ting	0
Ti-6Al-4V bare surface	Al 6 V 4 Ti Balance	0	0	0	0	0	0	0
A07075 bare surface		0	0	0	not analyzed	not analyzed	10	50

TABLE 2 (Continued)

	Composition	MgO	SrCO ₃	FS-01 40% MgCO ₃	FS-01 20% MgCO ₃	3110	SrO	KOH
A07050 bare surface		0	0	0	not analyzed	not analyzed	24	94
Graphite/Epoxy		0	0	0	0	0	0	0
Kevlar	Poly (p-phenylene- diamine-co- terephthalic) acid	0	0	0	0	0	0	0

Claims

1. An apparatus (10, 50, 60, 90) for suppressing a fire, having a gas generator (12) which generates a high temperature gas and having a passageway between said gas generator (12) and said fire, the apparatus (10, 50, 60, 90) characterized by:

said gas generator (12) containing a compacted mixture of:

a nitrogen rich powder fuel;
a powder oxidizer; and
a powder coolant (76),
and said high temperature gas generated by said gas generator (12) belonging to the group consisting of nitrogen, carbon dioxide, water vapor and mixtures thereof.

2. The apparatus (10, 50, 60, 90) of claim 1 further characterized by a flame suppressing material (72) initially disposed along said passageway so as to be driven by the high temperature gas to the fire.

3. An apparatus (10, 50, 60, 90) for suppressing a fire comprising

(a) a gas generator (12) containing a propellant (14);
(b) a chamber (20, 20', 92) containing a vaporizable liquid (18) or particles of a flame suppressing material (62) or a mixture of water (94) and ice (96);
(c) a passageway (26, 107) between said chamber (20, 20', 92) and said fire;
characterized by
(d) a passageway (22, 93) between said gas generator (12) and said chamber (20, 20', 92);
(e) said gas generator (12) containing a compacted mixture of:

a nitrogen rich powder fuel, a powder oxidizer, and a powder coolant; and generating a high temperature gas said high temperature gas belonging to the group consisting of nitrogen, carbon dioxide, water vapor and mixtures thereof.

4. The apparatus (10, 50, 60, 90) of claim 3 characterized in that said propellant (14) contains a mixture of a nitrogen rich fuel and an oxidizer.

5. The apparatus (10, 50, 60, 90) of claim 3 characterized in that said propellant (14) contains a mixture of a nitrogen rich fuel and an oxidizer in a fuel to oxidizer ratio, by weight, of from about 1:1 to about 1:2.

6. The apparatus (10, 50, 60, 70, 90) of any one of claims 2, 3, 4 or 5 characterized in that said flame suppressing material (62, 72) is selected from the group consisting of magnesium carbonate, magnesium hydroxide, calcium hydroxide, strontium hydroxide, barium hydroxide, aluminum hydroxide, potassium sulfate and mixtures thereof.

7. The apparatus (10, 50, 60, 90) of any one of claims 3, 4 or 5 characterized in that said vaporizable liquid (18) is selected from the group consisting of fluorocarbons, hydrogenated fluorocarbons, haloalkenes, carbon dioxide, water and mixtures thereof.

8. The apparatus (10, 50, 60, 90) of any one of claims 3, 4 or 5 characterized in that said vaporizable liquid (18) is a fluorocarbon having a boiling temperature below about -25°C and a room temperature vaporization pressure above about 0.17 MPa (25 psi).

9. The apparatus (10, 50, 60, 90) of any one of claims 3, 4 or 5 characterized in that said vaporizable liquid (18) is selected from the group consisting of water and carbon dioxide.

10. The apparatus (10, 50, 60, 70, 90) of any one of claims 2, 3, 4, 5 or 6 characterized in that the content of particles of the flame suppressing material (62, 72) is sufficient to inhibit the generation of corrosive effluent by-products.

11. The apparatus (10, 50, 60, 70, 90) of any one of claims 2 to 6 or 10 characterized in that said flame suppressing material (62, 72) contains from about 30% to about 60% by weight magnesium carbonate.

12. The apparatus (10, 50, 60, 70, 90) of any one of claims 1 to 11 **characterized in that** said gas generator contains an effective mixture of 5-aminotetrazole, strontium nitrate, clay and potassium 5-aminotetrazole.
13. The apparatus (50) of any one of claims 3 to 5 or 7 to 9 further including an elastomeric bladder (52).
14. The apparatus (10, 50, 60, 70, 90) of any one of claims 1 to 13 **characterized in that** said fuel is 5-aminotetrazole and said oxidizer is selected from the group consisting of strontium nitrate, potassium chlorate and mixtures thereof.
15. The apparatus (10, 50, 60, 90) of any one of claims 3 to 5 **characterized in that** said flame suppressing material (62) is selected from the group consisting of sodium bicarbonate, potassium bicarbonate, and mixtures thereof.
16. The apparatus (10, 50, 60, 90) of any one of claims 3 to 5 **characterized in that** said propellant (14) generates and effluent mixture of said high temperature gas and a solid particulate.
17. The apparatus (10, 50, 60, 70, 90) of any one of claims 1 to 16 **characterized in that** said high temperature gas has a temperature in excess of about 925°C and said mixture contains in excess of 20% by weight solid particulate.
18. The apparatus (10, 50, 60, 70, 90) of claim 16 or 17 **characterized in that** said solid particulate is MgO.
19. The apparatus (90) of any one of claims 3 to 5 or 7 to 9 further **characterized by** an outlet burst disc (104) in the passageway (107), said outlet burst disc (104) having a rupture pressure effective to cause said high temperature gas (98) to vaporize and superheat said water (94).
20. The apparatus (90) of claim 19 further **characterized by** a nozzle (100) configured to impinge said high temperature gas (98) and solid particulate on said mixture of water (94) and ice (96).
21. The apparatus (90) of claim 19 or 20 **characterized in that** an additive (108) effective to reduce the heat of fusion of said ice is present in said water.
22. The apparatus (90) of claim 21 **characterized in that** said additive (108) is selected from the group consisting of polyvinyl alcohol and methyl cellulose.
23. A gas generating composition comprising:
 - a nitrogen rich powder fuel;
 - a powder oxidizer; and
 - magnesium carbonate powder,wherein combustion of said nitrogen rich powder fuel, powder oxidizer and magnesium carbonate powder generates particulate and gas selected from the group consisting of nitrogen, carbon dioxide, water vapor, and mixtures thereof.
24. The gas generating composition of claim 23 **characterized in that** said fuel is 5-aminotetrazole and said oxidizer is strontium nitrate.
25. The gas generating composition of claim 23 or 24 **characterized in that** the magnesium carbonate content is from about 20% to 95% by weight.
26. The gas generating composition of any one of claims 23 to 25, **characterized in that** the magnesium carbonate content is from about 20% to about 70% by weight.
27. The gas generating composition of claim 23 **characterized by** comprising 30% to 60% magnesium carbonate by weight and on combustion producing magnesium oxide particulate and a high temperature gas comprising a mixture of nitrogen, carbon dioxide, and water vapor.
28. The gas generating composition of claim 23 **characterized in that** the magnesium carbonate content is at least 35 weight % of the composition.

29. The gas generating composition of any one of claims 23 to 28 **characterized in that** said nitrogen rich fuel and said oxidizer are mixed in a fuel to oxidizer ratio, by weight, of from about 1:1 to about 1:2.

30. The gas generating composition of any one of claims 23 to 29 **characterized in that** said fuel and said oxidizer and said magnesium carbonate are a compacted mixture of powders and, on average, the magnesium carbonate particles are larger than the fuel and oxidizer particles.

31. The gas generating composition of claim 25, **characterized in that** the magnesium carbonate content is 40% by weight.

Patentansprüche

1. Vorrichtung (10, 50, 60, 90) zum Löschen eines Feuers mit einem Gaserzeuger (12), der ein Hochtemperaturgas erzeugt, und mit einem Durchlassweg zwischen dem Gaserzeuger (12) und dem Feuer, wobei die Vorrichtung (10, 50, 60, 90) **dadurch gekennzeichnet ist, dass** der Gaserzeuger (12) ein verdichtetes Gemisch enthält aus einem stickstoffreichen pulverförmigen Brennstoff, einem pulverförmigen Oxidationsmittel, und einem pulverförmigen Kühlmittel (76), und dass das von dem Gaserzeuger (12) erzeugte Hochtemperaturgas zu der Gruppe gehört, die besteht aus Stickstoff, Kohlendioxid, Wasserdampf und Gemischen davon.

2. Vorrichtung (10, 50, 60, 90) nach Anspruch 1, außerdem **gekennzeichnet durch** ein Flammen löschendes Material (72), das anfänglich entlang dem Durchlassweg angeordnet ist, so dass es von dem Hochtemperaturgas auf das Feuer getrieben wird.

3. Vorrichtung (10, 50, 60, 90) zum Löschen eines Feuers aufweisend

- (a) einen Gaserzeuger (12), der ein Treibmittel (14) enthält,
- (b) eine Kammer (20, 20', 92), die eine verdampfbare Flüssigkeit (18) oder Teilchen eines Flammen löschenden Materials (62) oder ein Gemisch aus Wasser (94) und Eis (96) enthält,
- (c) einen Durchlassweg (26, 107) zwischen der Kammer (20, 20', 92) und dem Feuer, **gekennzeichnet durch**
- (d) einen Durchlassweg (22, 93) zwischen dem Gaserzeuger (12) und der Kammer (20, 20', 92),
- (e) wobei der Gaserzeuger (12) ein verdichtetes Gemisch enthält aus einem stickstoffreichen pulverförmigen Brennstoff, einem pulverförmigen Oxidationsmittel und einem pulverförmigen Kühlmittel, und ein Hochtemperaturgas erzeugt, das zu der Gruppe gehört, die besteht aus Stickstoff, Kohlendioxid, Wasserdampf und Gemischen davon.

4. Vorrichtung (10, 50, 60, 90) nach Anspruch 3, **dadurch gekennzeichnet, dass** das Treibmittel (14) ein Gemisch aus einem stickstoffreichen Brennstoff und einem Oxidationsmittel enthält.

5. Vorrichtung (10, 50, 60, 90) nach Anspruch 3, **dadurch gekennzeichnet, dass** das Treibmittel (14) ein Gemisch aus einem stickstoffreichen Brennstoff und einem Oxidationsmittel in einem Gewichtsverhältnis von Brennstoff zu Oxidationsmittel von etwa 1:1 bis etwa 1:2 enthält.

6. Vorrichtung (10, 50, 60, 70, 90) nach einem der Ansprüche 2, 3, 4 oder 5, **dadurch gekennzeichnet, dass** das Flammen löschende Material (62, 72) ausgewählt ist aus der Gruppe, die besteht aus Magnesiumcarbonat, Magnesiumhydroxid, Calciumhydroxid, Strontiumhydroxid, Bariumhydroxid, Aluminiumhydroxid, Kaliumsulfat und Gemischen davon.

7. Vorrichtung (10, 50, 60, 90) nach einem der Ansprüche 3, 4 oder 5, **dadurch gekennzeichnet, dass** die verdampfbare Flüssigkeit (18) ausgewählt ist aus der Gruppe, die besteht aus Fluorkohlenstoffen, hydrierten Fluorkohlenstoffen, Halogenalkanen, Kohlendioxid, Wasser und Gemischen davon.

8. Vorrichtung (10, 50, 60, 90) nach einem der Ansprüche 3, 4 oder 5,
dadurch gekennzeichnet, dass die verdampfbare Flüssigkeit (18) ein Fluorkohlenstoff ist mit einer Siedetempe-
ratur unterhalb etwa -25°C und einem Verdampfungsdruck bei Raumtemperatur von oberhalb etwa 0,17 MPa (25
psi).
9. Vorrichtung (10, 50, 60, 90) nach einem der Ansprüche 3, 4 oder 5,
dadurch gekennzeichnet, dass die verdampfbare Flüssigkeit (18) ausgewählt ist aus der Gruppe, die besteht
aus Wasser und Kohlendioxid.
10. Vorrichtung (10, 50, 60, 70, 90) nach einem der Ansprüche 2, 3, 4, 5 oder 6,
dadurch gekennzeichnet, dass der Gehalt an Teilchen des Flammen löschenden Materials (62, 72) ausreichend
ist, um die Erzeugung von korrosiven ausströmenden Nebenprodukten zu hemmen.
11. Vorrichtung (10, 50, 60, 70, 90) nach einem der Ansprüche 2 bis 6 oder 10,
dadurch gekennzeichnet, dass das Flammen löschende Material (62, 72) etwa 30 Gew.-% bis etwa 60 Gew.-%
Magnesiumcarbonat enthält.
12. Vorrichtung (10, 50, 60, 70, 90) nach einem der Ansprüche 1 bis 11,
dadurch gekennzeichnet, dass der Gaserzeuger ein wirksames Gemisch aus 5-Aminotetrazol, Strontiumnitrat,
Ton und Kalium-5-aminotetrazol enthält.
13. Vorrichtung (50) nach einem der Ansprüche 3 bis 5 oder 7 bis 9,
die außerdem eine elastomere Blase (52) enthält.
14. Vorrichtung (10, 50, 60, 70, 90) nach einem der Ansprüche 1 bis 13,
dadurch gekennzeichnet, dass der Brennstoff 5-Aminotetrazol ist und das Oxidationsmittel ausgewählt ist aus
der Gruppe, die besteht aus Strontiumnitrat, Kaliumchlorat und Gemischen davon.
15. Vorrichtung (10, 50, 60, 90) nach einem der Ansprüche 3 bis 5,
dadurch gekennzeichnet, dass das Flammen löschende Material (62) ausgewählt ist aus der Gruppe, die besteht
aus Natriumbicarbonat, Kaliumbicarbonat und Gemischen davon.
16. Vorrichtung (10, 50, 60, 90) nach einem der Ansprüche 3 bis 5,
dadurch gekennzeichnet, dass das Treibmittel (14) ein ausströmendes Gemisch aus dem Hochtemperaturgas
und einem teilchenförmigen Feststoff erzeugt.
17. Vorrichtung (10, 50, 60, 70, 90) nach einem der Ansprüche 1 bis 16,
dadurch gekennzeichnet, dass das Hochtemperaturgas eine Temperatur oberhalb etwa 925°C hat und das Ge-
misch mehr als 20 Gew.-% teilchenförmigen Feststoff enthält.
18. Vorrichtung (10, 50, 60, 70, 90) nach Anspruch 16 oder 17,
dadurch gekennzeichnet, dass der teilchenförmige Feststoff MgO ist.
19. Vorrichtung (90) nach einem der Ansprüche 3 bis 5 oder 7 bis 9,
außerdem gekennzeichnet durch eine Auslass-Platzmembran (104) in dem Durchlassweg (107), wobei die Aus-
lass-Platzmembran (104) einen Bruchdruck hat, der dahingehend wirksam ist, das Hochtemperaturgas (98) dazu
zu veranlassen, zu verdampfen und das Wasser (94) zu überhitzen.
20. Vorrichtung (90) nach Anspruch 19,
außerdem gekennzeichnet durch eine Düse (100), die so gestaltet ist, dass das Hochtemperaturgas (98) und
der teilchenförmige Feststoff auf das Gemisch aus Wasser (94) und Eis (96) auftreffen.
21. Vorrichtung (90) nach Anspruch 19 oder 20,
dadurch gekennzeichnet, dass in dem Wasser ein Zusatzstoff (108) vorhanden ist, der dahingehend wirksam
ist, die Schmelzwärme des Eises zu verringern.
22. Vorrichtung (90) nach Anspruch 21,
dadurch gekennzeichnet, dass der Zusatzstoff (108) ausgewählt ist aus der Gruppe, die besteht aus Polyvinyl-

alkohol und Methylcellulose.

23. Gas erzeugende Zusammensetzung aufweisend
einen stickstoffreichen pulverförmigen Brennstoff,
ein pulverförmiges Oxidationsmittel, und
Magnesiumcarbonat-Pulver,
wobei die Verbrennung des stickstoffreichen pulverförmigen Brennstoffs, des pulverförmigen Oxidationsmittels
und des Magnesiumcarbonat-Pulvers Teilchen und Gas, das ausgewählt ist aus der Gruppe, die besteht aus Stick-
stoff, Kohlendioxid, Wasserdampf und Gemischen davon, erzeugt.
24. Gas erzeugende Zusammensetzung nach Anspruch 23,
dadurch gekennzeichnet, dass der Brennstoff 5-Aminotetrazol ist und das Oxidationsmittel Strontiumnitrat ist.
25. Gas erzeugende Zusammensetzung nach Anspruch 23 oder 24,
dadurch gekennzeichnet, dass der Magnesiumcarbonat-Gehalt etwa 20 bis 95 Gew.-% beträgt.
26. Gas erzeugende Zusammensetzung nach einem der Ansprüche 23 bis 25,
dadurch gekennzeichnet, dass der Magnesiumcarbonat-Gehalt etwas 20 bis etwa 70 Gew.-% beträgt.
27. Gas erzeugende Zusammensetzung nach Anspruch 23,
dadurch gekennzeichnet, dass sie 30 Gew.-% bis 60 Gew.-% Magnesiumcarbonat aufweist und bei der Ver-
brennung Magnesiumoxid-Teilchen und ein Hochtemperaturgas, das ein Gemisch aus Stickstoff, Kohlendioxid
und Wasserdampf aufweist, erzeugt.
28. Gas erzeugende Zusammensetzung nach Anspruch 23,
dadurch gekennzeichnet, dass der Magnesiumcarbonat-Gehalt mindestens 35 Gew.-% der Zusammensetzung
beträgt.
29. Gas erzeugende Zusammensetzung nach einem der Ansprüche 23 bis 28,
dadurch gekennzeichnet, dass der stickstoffreiche Brennstoff und das Oxidationsmittel in einem Gewichtsver-
hältnis von Brennstoff zu Oxidationsmittel von etwa 1:1 bis etwa 1:2 gemischt sind.
30. Gas erzeugende Zusammensetzung nach einem der Ansprüche 23 bis 29,
dadurch gekennzeichnet, dass der Brennstoff und das Oxidationsmittel und das Magnesiumcarbonat ein ver-
dichtetes Gemisch von Pulvern sind und dass, im Mittel, die Magnesiumcarbonat-Teilchen größer sind als die
Brennstoff- und Oxidationsmittel-Teilchen.
31. Gas erzeugende Zusammensetzung nach Anspruch 25,
dadurch gekennzeichnet, dass der Magnesiumcarbonat-Gehalt 40 Gew.-% beträgt.

Revendications

1. Appareil (10, 50, 60, 90) pour supprimer un feu, présentant un générateur de gaz (12) qui produit un gaz à tem-
pérature élevée et ayant une voie de passage entre ledit générateur de gaz (12) et ledit feu, l'appareil (10, 50, 60,
90) étant caractérisé par ;

ledit générateur de gaz (12) contenant un mélange compacté de:

un carburant pulvérulent riche en azote ;
un oxydant pulvérulent ; et
un réfrigérant pulvérulent (76),
et ledit gaz à température élevée produit par ledit générateur de gaz (12) étant choisi parmi l'azote, le
dioxyde de carbone, la vapeur d'eau et des mélanges de ceux-ci.
2. Appareil (10, 50, 60, 90) selon la revendication 1, caractérisé en outre par une matière supprimant les flammes
(72) initialement déposée le long de ladite voie de passage afin d'être conduite par le gaz à température élevée
vers le feu.

3. Appareil (10, 50, 60, 90) pour supprimer un feu comprenant

- (a) un générateur de gaz (12) contenant un agent de propulsion (14) ;
- (b) une chambre (20, 20', 92) contenant un liquide vaporisable (18) ou des particules d'une matière supprimant les flammes (62) ou un mélange d'eau (94) et de glace (96) ;
- (c) une voie de passage (26, 107) entre ladite chambre (20, 20', 92) et ledit feu ;
caractérisé par
- (d) une voie de passage (22, 93) entre ledit générateur de gaz (12) et la dite chambre (20, 20', 92) ;
- (e) ledit générateur de gaz (12) contenant un mélange compacté de :

un carburant pulvérulent riche en azote, un oxydant pulvérulent et un réfrigérant pulvérulent ; et produisant un gaz à température élevée, ledit gaz à température élevée étant choisi parmi l'azote, le dioxyde de carbone, la vapeur d'eau et des mélanges de ceux-ci.

- 4. Appareil (10, 50, 60, 90) selon la revendication 3, **caractérisé en ce que** ledit agent de propulsion (14) contient un mélange d'un carburant riche en azote et d'un oxydant.
- 5. Appareil (10, 50, 60, 90) selon la revendication 3, **caractérisé en ce que** ledit agent de propulsion (14) contient un mélange d'un carburant riche en azote et d'un oxydant dans un rapport carburant à oxydant en poids compris entre environ 1:1 et environ 1:2.
- 6. Appareil (10, 50, 60, 70, 90) selon l'une quelconque des revendications 2, 3, 4 ou 5, **caractérisé en ce que** ladite matière supprimant les flammes (62, 72) est choisie parmi le carbonate de magnésium, l'hydroxyde de magnésium, l'hydroxyde de calcium, l'hydroxyde de strontium, l'hydroxyde de baryum, l'hydroxyde d'aluminium, le sulfate de potassium et des mélanges de ceux-ci.
- 7. Appareil (10, 50, 60, 90) selon l'une quelconque des revendications 3, 4 ou 5, **caractérisé en ce que** ledit liquide vaporisable (18) est choisi parmi des fluorocarbones, des fluorocarbones hydrogénés, des haloalcènes, le dioxyde de carbone, l'eau et des mélanges de ceux-ci.
- 8. Appareil (10, 50, 60, 90) selon l'une quelconque des revendications 3, 4 ou 5, **caractérisé en ce que** ledit liquide vaporisable (18) est un fluorocarbonate ayant une température d'ébullition inférieure à environ -25°C et une pression de vaporisation à température ambiante supérieure à environ 0,17 MPa (25 psi).
- 9. Appareil (10, 50, 60, 90) selon l'une quelconque des revendications 3, 4 ou 5, **caractérisé en ce que** ledit liquide vaporisable (18) est choisi parmi l'eau et le dioxyde de carbone.
- 10. Appareil (10, 50, 60, 70, 90) selon l'une quelconque des revendications 2, 3, 4, 5 ou 6, **caractérisé en ce que** la teneur des particules de la matière supprimant les flammes (62, 72) est suffisante pour inhiber la production de produits secondaires d'effluents corrosifs.
- 11. Appareil (10, 50, 60, 70, 90) selon l'une quelconque des revendications 2 à 6 ou 10, **caractérisé en ce que** ladite matière supprimant les flammes (62, 72) contient d'environ 30 % à environ 60 % en poids de carbonate de magnésium.
- 12. Appareil (10, 50, 60, 70, 90) selon l'une quelconque des revendications 1 à 11, **caractérisé en ce que** ledit générateur de gaz contient un mélange efficace de 5-aminotétrazole, de nitrate de strontium, d'argile et de 5-aminotétrazole de potassium.
- 13. Appareil (50) selon l'une quelconque des revendications 3 à 5 ou 7 à 9 comprenant en outre une vessie chauffante élastomère (52).
- 14. Appareil (10, 50, 60, 70, 90) selon l'une quelconque des revendications 1 à 13, **caractérisé en ce que** ledit carburant est le 5-aminotétrazole et ledit oxydant est choisi parmi le nitrate de strontium, le chlorate de potassium et des mélanges de ceux-ci.
- 15. Appareil (10, 50, 60, 90) selon l'une quelconque des revendications 3 à 5, **caractérisé en ce que** ladite matière supprimant les flammes (62) est choisie parmi le bicarbonate de sodium, le bicarbonate de potassium et des

mélanges de ceux-ci.

16. Appareil (10, 50, 60, 90) selon l'une quelconques des revendications 3 à 5, **caractérisé en ce que** ledit agent de propulsion (14) produit un mélange d'effluents dudit gaz à température élevée et d'une matière particulaire solide.
17. Appareil (10, 50, 60, 70, 90) selon l'une quelconque des revendications 1 à 16, **caractérisé en ce que** ledit gaz à température élevée présente une température excédant environ 925°C et ledit mélange contient plus de 20 % en poids de matière particulaire solide.
18. Appareil (10, 50, 60, 70, 90) selon la revendication 16 ou 17, **caractérisé en ce que** ladite matière particulaire solide est MgO.
19. Appareil (90) selon l'une quelconque des revendications 3 à 5 ou 7 à 9, **caractérisé en outre par** un diaphragme d'éclatement de sortie (104) dans la voie de passage (107), ledit diaphragme d'éclatement de sortie (104) ayant une pression de rupture efficace pour occasionner le fait que ledit gaz à température élevée (98) se vaporise et surchauffe ladite eau (94).
20. Appareil (90) selon la revendication 19, **caractérisé en outre par** un injecteur (100) configuré pour injecter ledit gaz à température élevée (98) et ladite matière particulaire solide sur ledit mélange d'eau (94) et de glace (96).
21. Appareil (90) selon la revendication 19 ou 20, **caractérisé en ce qu'un** additif (108) efficace pour réduire la chaleur de fusion de ladite glace est présent dans ladite eau.
22. Appareil (90) selon la revendication (21), **caractérisé en ce que** ledit additif (108) est choisi parmi le poly(alcool vinylique) et la méthylcellulose.
23. Composition génératrice de gaz comprenant :
 - un carburant pulvérulent riche en azote ;
 - un oxydant pulvérulent ; et
 - une poudre de carbonate de magnésium,dans laquelle la combustion dudit carburant pulvérulent riche en azote, de l'oxydant pulvérulent et de la poudre de carbonate de magnésium produit une matière particulaire et un gaz choisi parmi l'azote, le dioxyde de carbone, la vapeur d'eau et des mélanges de ceux-ci.
24. Composition génératrice de gaz selon la revendication 23, **caractérisée en ce que** ledit carburant est le 5-aminotétrazole et ledit oxydant est le nitrate de strontium.
25. Composition génératrice de gaz selon la revendication 23 ou 24, **caractérisée en ce que** la teneur en carbonate de magnésium est comprise entre environ 20 % et 95 % en poids.
26. Composition génératrice de gaz selon l'une quelconque des revendications 23 à 25, **caractérisée en ce que** la teneur en carbonate de magnésium est comprise entre environ 20 % et environ 70 % en poids.
27. Composition génératrice de gaz selon la revendication 23, **caractérisée en ce qu'elle** comprend de 30 % à 60 % de carbonate de magnésium en poids et **en ce qu'elle** produit par combustion une matière particulaire d'oxyde de magnésium et un gaz à température élevée comprenant un mélange d'azote, de dioxyde de carbone et de vapeur d'eau.
28. Composition génératrice de gaz selon la revendication 23, **caractérisée en ce que** la teneur en carbonate de magnésium est d'au moins 35 % en poids de la composition.
29. Composition génératrice de gaz selon l'une quelconque des revendications 23 à 28, **caractérisée en ce que** ledit carburant riche en azote et ledit oxydant sont mélangés dans un rapport carburant à oxydant en poids d'environ 1:1 à environ 1:2.
30. Composition génératrice de gaz selon l'une quelconque des revendications 23 à 29, **caractérisée en ce que** ledit

EP 0 705 120 B1

carburant et ledit oxydant et ledit carbonate de magnésium sont un mélange compacté de poudres et que les particules de carbonate de magnésium sont en moyenne plus grandes que les particules de carburant et d'oxydant.

- 5 31. Composition génératrice de gaz selon la revendication 25, caractérisée en ce que la teneur en carbonate de magnésium est de 40 % en poids.

10

15

20

25

30

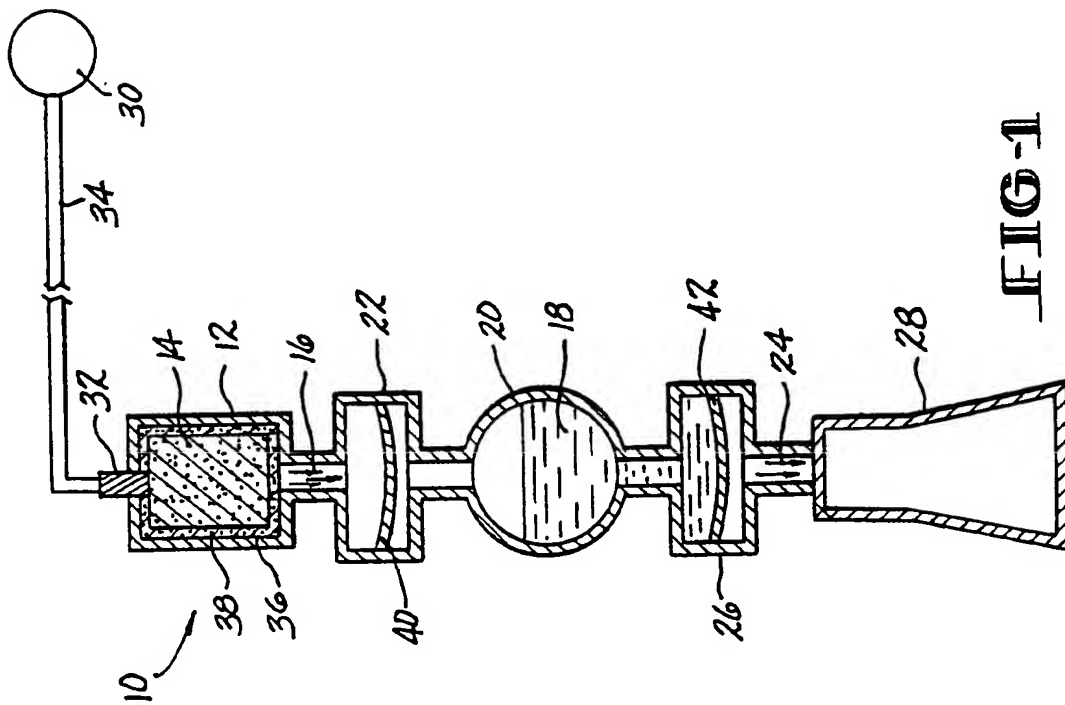
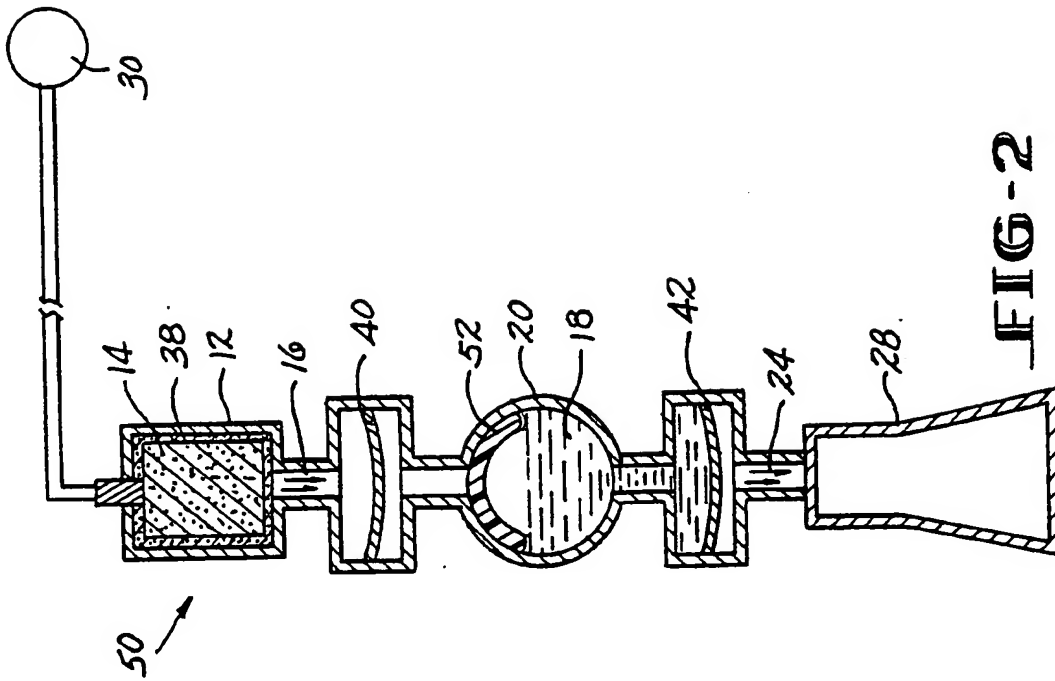
35

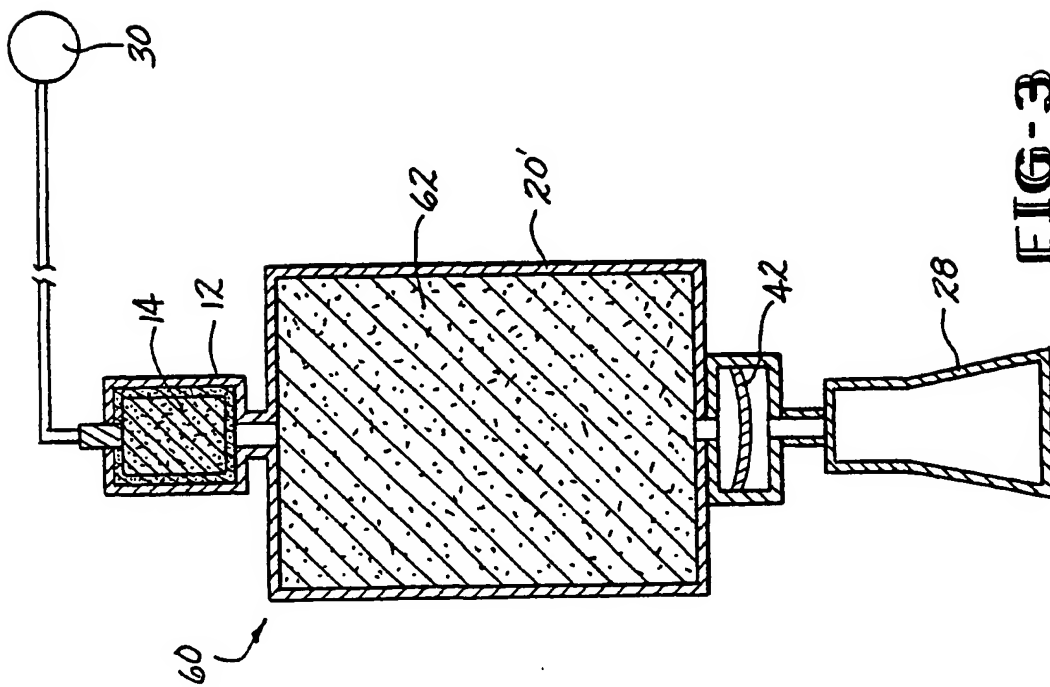
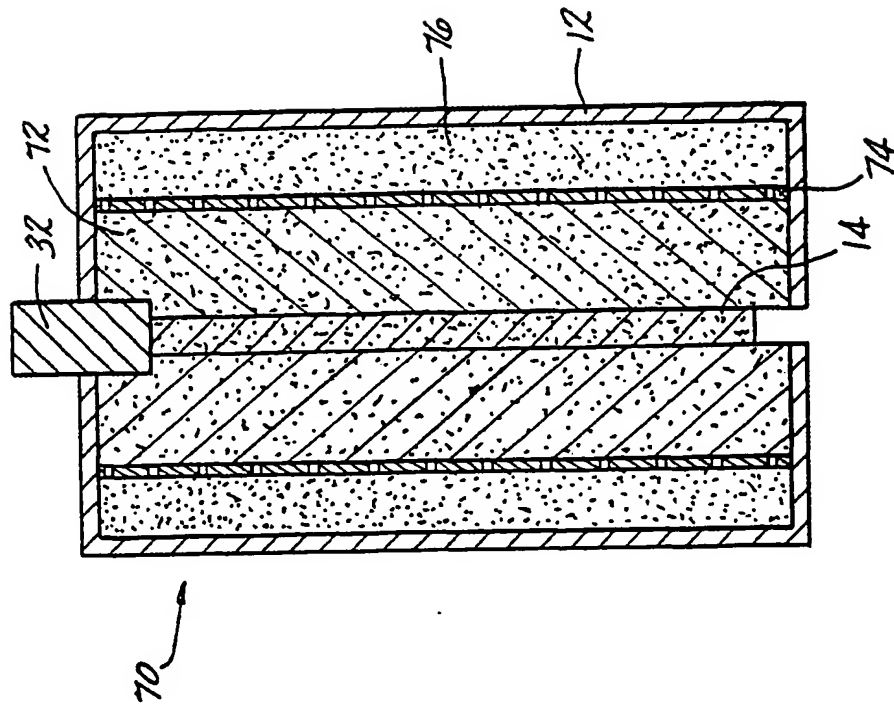
40

45

50

55





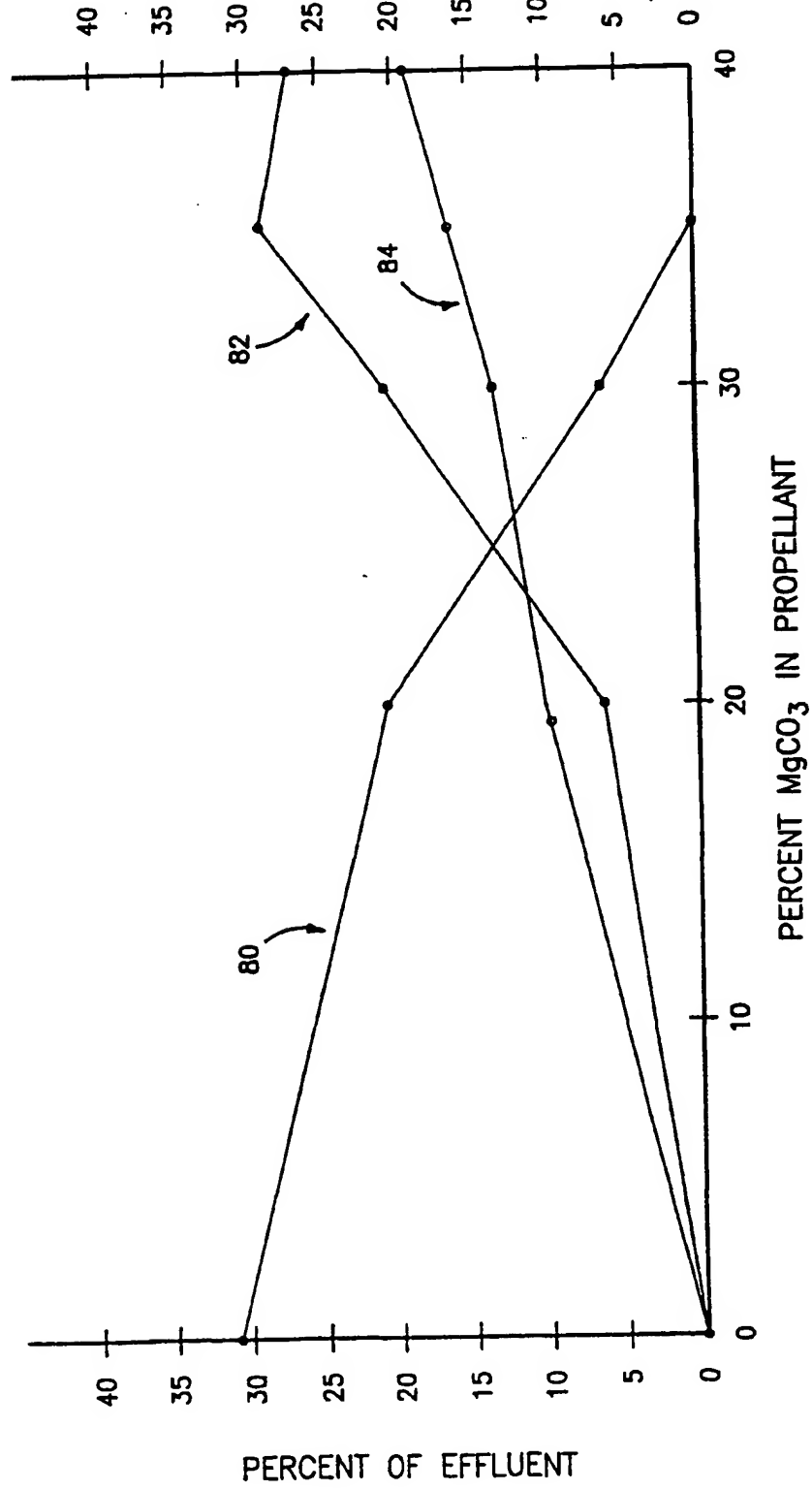


FIG-5

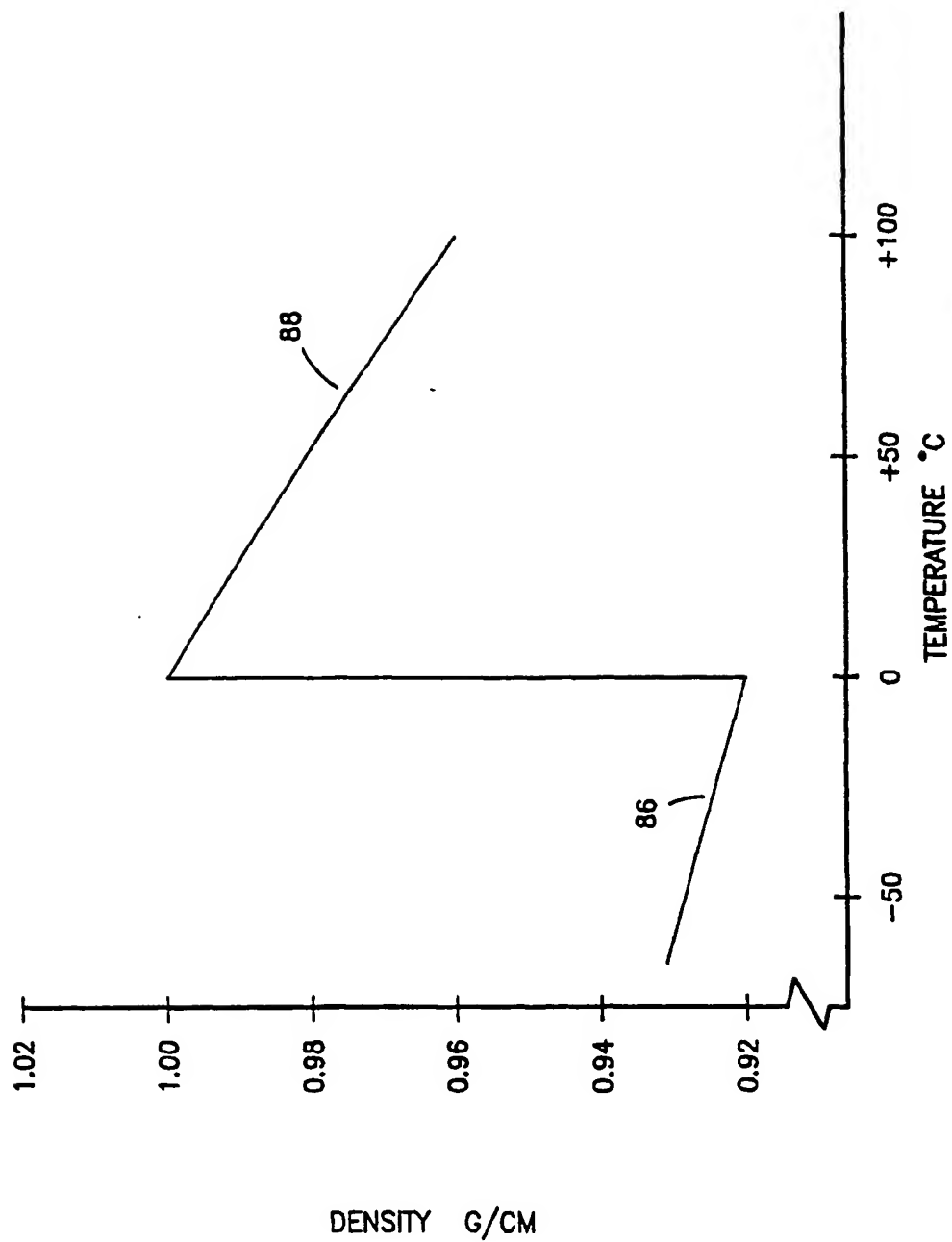


FIG-6

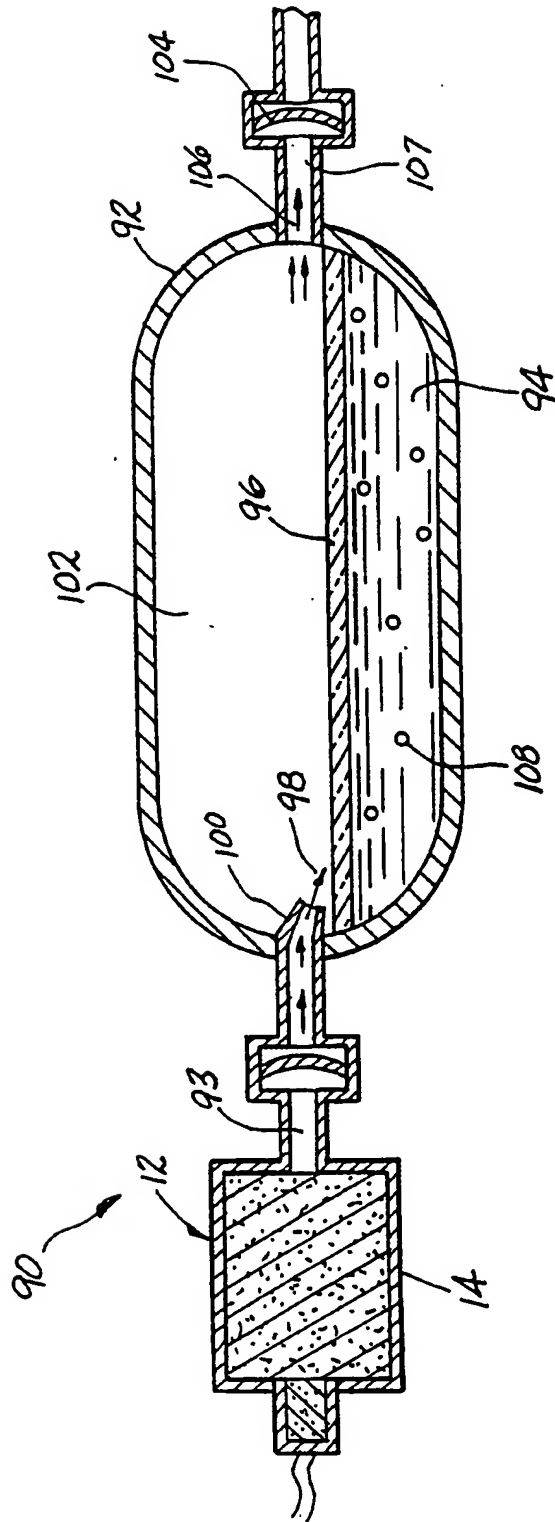


FIG-7